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Intra-Monolayer Hydrogen-Bonding in Monolayer Protected Gold Clusters

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ABSTRACT

Unlike the highly ordered Self-Assembled Monolayers (SAMs) formed on flat gold surfaces, those on gold nanoparticles radiate from a roughly spherical center and are amorphous in structure. One result of this structural motif is that the strength of *intra*-monolayer non-covalent interactions, such as π-stacking and hydrogen bonding, are a function of the distance of the recognition element from the colloidal core. We present here an exploration of these phenomena in amide functionalized thiols in MPCs where the amide functionality position was varied in the alkane chain. [1]

INTRODUCTION

Self-Assembled Monolayers (SAM) of organic molecules on flat surfaces are well known to form highly-ordered, semi-crystalline phases.[2] SAMs on nanoparticles, or Monolayer Protected Clusters (MPCs) [3] are less ordered as they radiate from a highly faceted, roughly spherical surface. Here, order is decreased as a function of distance from the nanoparticle core (Figure **1**).[4] This variable degree of order will have a strong impact on the design and fabrication of nanoscale devices based on functional organic components in the monolayer.[5] To explore this phenomena, we have prepared a series of amide functionalized MPCs (Figure **2**) and investigated the nature of both *intra*- and *inter*-monolayer hydrogen bonding in the solid and solution phases.

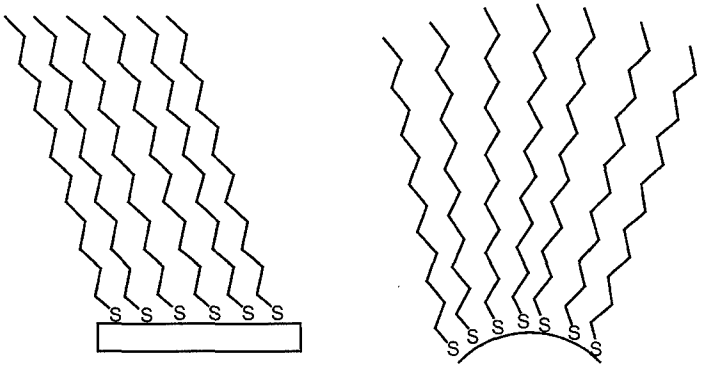

Figure 1. Monolayer structure on (left) flat and (right) colloidal surfaces.

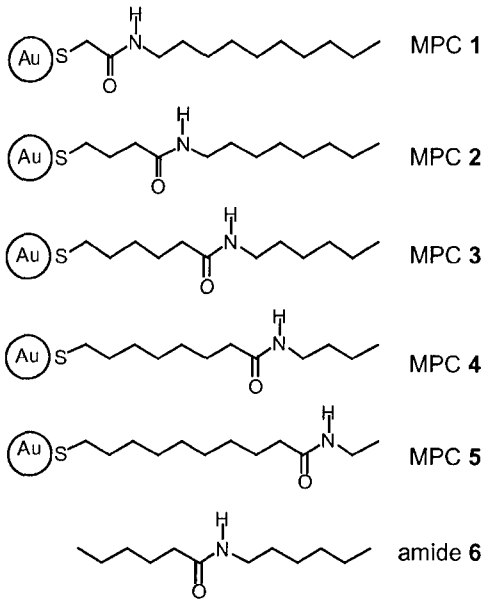

Figure 2. MPCs **1** - **5** and amide **6**.

EXPERIMENTAL DETAILS

Synthesis of amide functionalized thiols, which typically involved acylation various alkyl amines with ω-haloacid chlorides followed by halogen displacement with potassium thiol acetate and acyl protection group removal with methoxide, was described fully earlier.[1] These thiols were then used in the standard two-phase Brust reaction to yield the desired MPCs.[6] All MPCs behaved in a manor typical for alkane monolayers, except MPC **5** which precipitated out during its synthesis, likely due to the high polarity of the near-terminal amide groups. Finally, amide **6** was also prepared to provide a non-monolayer reference compound.

IR spectra were recorded either as thin films cast on NaCl plates from CH_2Cl_2 or as CH_2Cl_2 solutions in a CaF_2 solution IR cell. 1H NMR spectra were recorded in K_2CO_3 neutralized $CDCl_3$ and referenced to TMS (δ = 0.0 ppm) as an internal standard. TEM samples were prepared by placing one drop of the desired MPC solutions (1 mg/mL in CH_2Cl_2) on a 300 mesh Cu grid with a carbon film. Samples were then analyzed on a JEOL 100CX TEM using an acceleration voltage of 100 keV.

DISCUSSION

Hydrogen bonding was initially investigated in films of MPCs. (Figure **3**) Here, a general trend in decreased hydrogen bonding efficiency is observed for the series of MPCs **2** to **5**, with a gradual increase in the NH stretching frequency from 3290 cm^{-1} to 3294 cm^{-1}. In sharp contrast, a significant decrease in hydrogen bonding is exhibited by MPC **1**, with a NH stretching frequency of 3300 cm^{-1}. Amide thiols on flat gold surfaces, by comparisons, typically exhibit NH stretching frequencies of *ca.* 3293 cm^{-1}.[7] Further comparison can be made to films of amide **6**, known to be hydrogen bonded in the solid state, where the NH stretch occurs at 3286 cm^{-1}. The amide II region of the IR also provides insight into hydrogen bonding.[8] Non-hydrogen bound amides typically exhibit a peak at 1510 cm^{-1}, and a substantial shift to lower wave-numbers for MPC **1** is again indicative of decreased hydrogen bonding relative to the other MPCs. (Figure **3**)

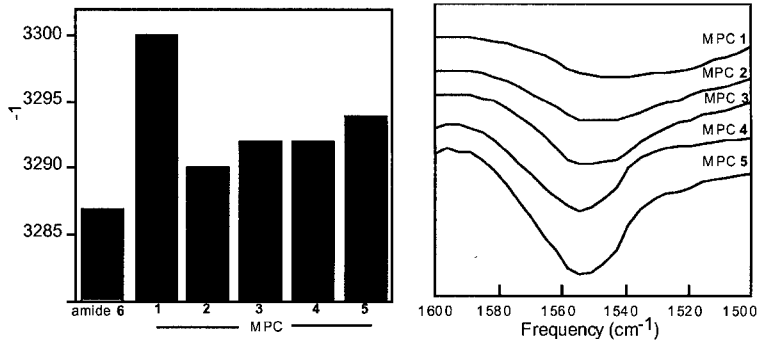

Figure 3. Left: NH stretching frequency of amide **6** and MPCs **1 - 5** as thin films. Right: IR spectra of the Amide II region for the same compounds.

Since MPC monolayers are well known to interdigitate in the solid state,[9] hydrogen bonding was also investigated in solution to confirm that *intra*-monolayer interactions predominate. In CH_2Cl_2 solutions, a similar trend of NH bond stretching was observed: MPC **1** was found to be the least hydrogen-bound (ν_{NH} = 3302 cm^{-1}), followed by an initial increase then gradual decrease in the hydrogen bonding in MPCs **2** to **5**. In solution, the NH stretch of amide **6** occurred at 3446 cm^{-1}, and is indicative of negligible hydrogen bonding. Further, ^{1}H NMR confirmed this result in that the chemical shift of the amide NH proton moved upfield from 8.15 ppm (MPC **2**) to 7.7 ppm (MPC **5**), again indicating a decrease in hydrogen bonding when the distance from the core surface is increased.[10] These results are readily compared to amide **6**, where the amide NH proton is observed at 5.6 ppm. Neither the NH stretching frequency or chemical shift was significantly effected by a 10-fold dilution, indicating a low chance that the spectral shifts are a result of *inter*-monolayer hydrogen bonding (Figure **4**). Further, these experiments point out a more significant distance dependence trend in hydrogen bonding as a function of surface distance.

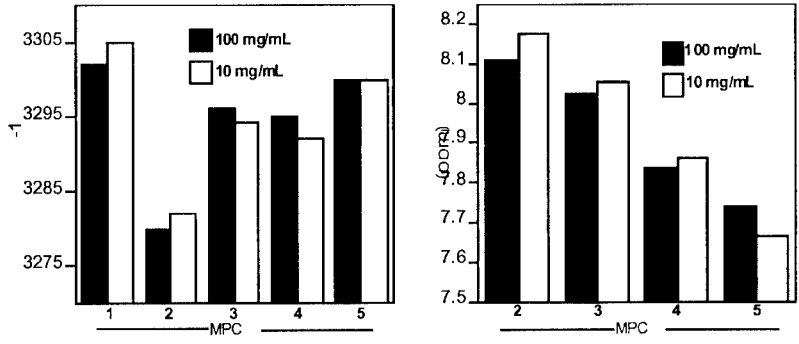

Figure 4. Left: NH stretching frequency of MPCs **1** - **5** as CH_2Cl_2 solutions at concentrations of 100 and 10 mg/mL. Right: NH chemical shift from the ^1H NMR spectra of MPCs **2** - **5** as $CDCl_3$ solutions at concentrations of 100 and 10 mg/mL.

These results can be rectified upon consideration of the radial nature of the monolayer structure. Close to the surface, as for MPC **1**, there is a high amount of steric congestion, and this likely leads to the inability of the amide groups to adopt an ideal configuration. Close packing is overcome for MPC **2**, where the strongest hydrogen bonding is observed. As the amide group is moved further from the inorganic core, MPCs **3** - **5**, an increase in monolayer disorder makes hydrogen bonding entropically unfavorable.

Transmission Electron Microscopy (TEM) can provide insight to *inter*-monolayer hydrogen bonding interactions as this should lead to the formation of nanoparticle aggregates. In the case of MPCs **1** - **4**, no aggregation is observed (Figure **5**). TEMs of MPC **5**, however, reveal the presence of several large (hundreds of nanometers in size) aggregates. These structures are likely a result of strengthened interdigitation as a result of *inter*-monolayer amide hydrogen bonding (Figure **6**).

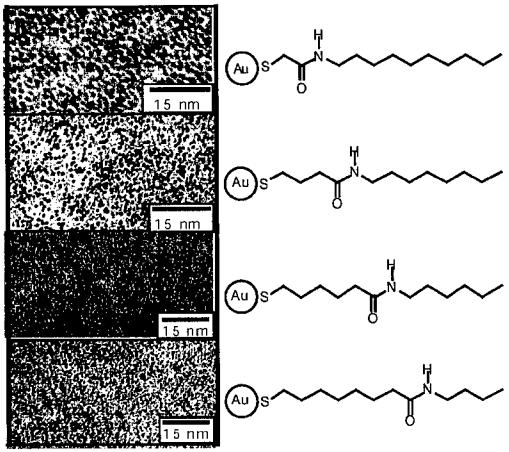

Figure 5. TEM micrographs of MPCs **1** - **4**.

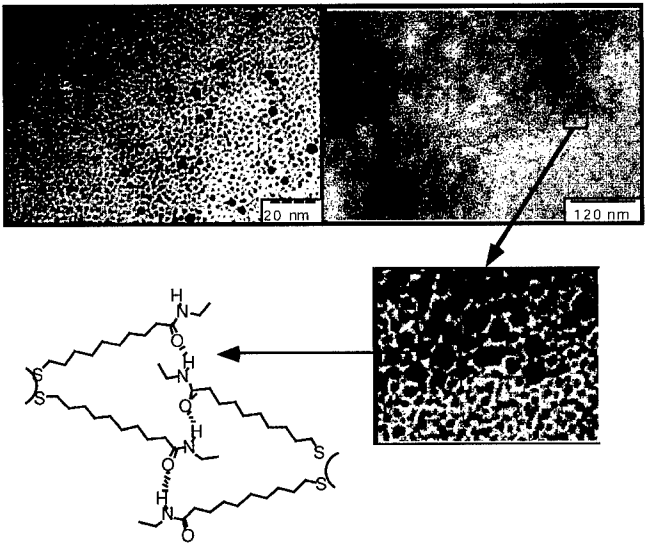

Figure 6. TEM micrographs of MPCs **5**. Top left: an unaggregated region showing particles of both *ca.* 2 and *ca.* 6 nm diameter. Top right: a low magnification view of an aggregated region and, bottom right, a magnification of the region indicated by the box. Bottom left: depiction of the proposed *inter*-monolayer hydrogen bonding responsible for aggregation.

CONCLUSIONS

In summary, a series of MPCs bearing amide containing monolayers has been prepared. In this series, the amide linkage was systematically moved along the alkane chain to provide the ability to study the strength of *inter*- and *intra*-monolayer hydrogen bonding interactions as a function of distance from the gold core. It was found that when the amide group was in extreme proximity to the core surface, steric crowding prohibited extensive hydrogen bonding interactions. This was followed by an increase in interactions when steric congestion could be overcome, and a slow decline in hydrogen bonding as the amide was moved further away from the surface. Near terminal amide groups were also found to participate in *inter*-monolayer interactions in the solid state, as evidenced by aggregation observed in TEM. These findings are consistent with the radial nature of monolayer structure in MPCs.

ACKNOWLEDGMENTS

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